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Modulating the magnetic relaxation of lanthanide-based single-molecule magnets

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In the area of molecular magnetism, single molecule magnets (SMMs) containing lanthanide elements are of immense scientific and technological interest because of their large energy barriers and high measured hysteresis temperature. Although there has been significant progress in the synthesis and characterization of lanthanide-based SMMs, there are still challenges, for instance, how single-ion anisotropy of lanthanide elements can be exploited, and how zero-field tunneling of magnetization can be suppressed. This article is devoted to the progress in various methodologies for modulating magnetic relaxation, especially in terms of crystal field and magnetic interactions. The crystal field plays a dominant role in creating single-molecule magnets with largely anisotropic f-elements, while the strong coupling between magnetic centers is able to suppress quantum tunneling of magnetization efficiently.

lanthanide, single-molecule magnets, relaxation dynamics, quantum tunneling, magnetic coupling

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Magnetic materials are exploited extensively in our everyday life, ranging from classical information-storing applications to the recent magnetocaloric and medical materials [1,2]. As a promising nanomagnetic material, single-molecule magnets (SMMs) [3] have flourished because of their potential for application in high-density information storage [4,5], quantum computing [6] and molecule spintronics [7,8]. It is well known that these SMMs have a large high-spin ground state (S) in combination with a large easy-axis type magnetic anisotropy (D), presenting slow relaxation of the magnetization of purely molecular origin [9]. It has been nearly twenty years since the first discovery that the Mn_{12} cluster with a bistable ground state shows slow magnetic relaxation. Initially, most efforts were dedicated to obtaining high-spin, strongly-coupled transition-metal SMMs such as the Mn_{12} derivatives [9,10] and Fe_8 iron complexes [11]. However, theoretical study based on experiments suggests that large magnetic anisotropy is not helped by a high spin state of the ground state for transition-metal systems, which has been a crucial roadblock to obtaining systems with larger energy barriers [12,13]. Nevertheless, since Ishikawa et al. [14] discovered lanthanide double-decker complexes $[Pc_2Ln]^-TBA^+$ (Ln = Tb^{III}, Dy^{III}, Ho^{III}; $TBA^+ = N(C_4H_9)^+$) functioning as very efficient SMMs, the complexes containing lanthanide elements are highlighted and large numbers of Lanthanide-based Single Molecule Magnets (Ln-SMMs) with larger energy barriers have evolved, especially Dy-based complexes with various nuclearities from Dy_1 [15], Dy_2 [16,17], Dy_3 [18,19], Dy_4 [20,21], Dy_6 [22], Dy_{10} [23] to Dy_{26} [24]. These systems may hold the key to obtaining high anisotropic barrier single-molecule magnets (SMMs).

Because of the effective shielding of the 4f electrons by the outer $5s^2$ and $5p^6$ shells of the Xe core, lanthanide ions are characterized by large unquenched orbital angular momentum, with the spin-orbit coupled ground state of $^{2S+1}L_J$

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[25]. This leads to a weak expected coupling interaction involving the f electrons, which would not give many opportunities to achieve really large spin values in a well isolated ground state. However, strong single-ion anisotropy associating with slow relaxation compensates for this drawback [26]. Moreover, the simplified spin Hamiltonian approaches which have been useful for interpreting the magnetism of most transition metal complexes cannot be used in lanthanide-based complexes [27]. The mechanisms involved in pure 4f systems are very difficult to grasp. Because of the complexity of lanthanide ions, modulating the magnetic relaxation of lanthanide-based complexes presents a formidable challenge. Nevertheless, remarkable progress is being made regarding the synthesis and characterization of lanthanide-based SMMs [28,29] and the investigation of the relaxation mechanism reveals two main factors: Single-ion anisotropy [30], determined by the strength and symmetry of the local crystal field, is probably the most important factor; in addition, the magnetic (Ising-typed exchange or dipolar) interaction between magnetic centers is a secondary consideration in modulating magnetic relaxation [31].

1 Crystal field

Although the crystal-field effect is generally smaller than the spin-orbit coupling energy, it turns out to be a key factor in creating single-molecule magnets with f-elements, because the local anisotropy of the lanthanide ion can be influenced strongly by the coordination geometry [32]. Indeed, ligand fields with a high-order single axis $C_n (n > 2)$ could split the $(2J+1)$ degenerate ground states into new sublevels, which would exploit the single ion anisotropy for individual f-elements, thus giving rise to a high energy barrier for relaxation [15]. For instance, the first SMMs containing lanthanide elements, $[Pc_2Ln]^-$, display unprecedented relaxation behavior in contrast to transition-metal SMMs, where the local symmetry of D_{4d} has been demonstrated through choosing planar phthalocyanine ligand. Recently, an organometallic complex made up of an erbium atom sandwiched between two different aromatic hydrocarbon rings, (Cp*)Er(COT) (Cp* = $C_5Me_5^-$; COT = $C_8H_8^{2-}$), where the Er(III) ion is situated in a low-symmetry coordination sphere environment with the overall symmetry of the molecule being C_s, has been reported to exhibit unique magnetic behavior with energy barrier as high as 320 K with $\tau_0 = 8.17\times10^{-11}$ s [33]. The ligand field analysis with symmetry of $C_{\infty v}$ reveals an Ising-type ground state. However, the Ising nature of the molecule needs to be further confirmed by single crystal data due to the approximation [33]. Further, more flexible polydentate ligands could be applied for the polynuclear Lanthanide-based SMMs [34,35]. Consequently, the complicated multiple relaxation processes, which are most likely associated with distinct anisotropic centers due to the different crystal field environments, have been increasingly identified in a weakly coupled lanthanide system [20,21]. It is therefore possible to "fine-tune" the magnetic properties of lanthanide complexes through the alteration of different ligand fields.

To probe how the ligand field affects the relaxation behavior of the magnetization of Ln-SMMs, it would be helpful to focus on the most simple mononuclear SMMs, Pc_2Ln and LnPOM.

As the first discovered Lanthanide-based SMM, the magnetic properties of the double-decker complexes $[Pc_2Ln]^-$ have been intensively investigated including their dynamic magnetic properties [36] and the characteristic sublevel structures of their ground multiplets [37]. In Figure 1(a), the structure of the phthalocyanine complex is shown. The central lanthanide ion is coordinated by eight nitrogen atoms of the two phthalocyaninato moieties with approximate D_{4d} symmetry [38]. The high-order axial coordination field promotes the single ion anisotropy of lanthanide ions, leading to an easy axis of the magnetization.

Figure 2(a) shows the temperature dependences of the AC susceptibilities of the $[Pc_2Tb]^-$ complex [14]. Out-of-phase (χ'') signals are observed with a maximum of up to 40 K for 997 Hz, indicating the strong relaxation behavior of magnetization. For a diluted sample, the peaks of the

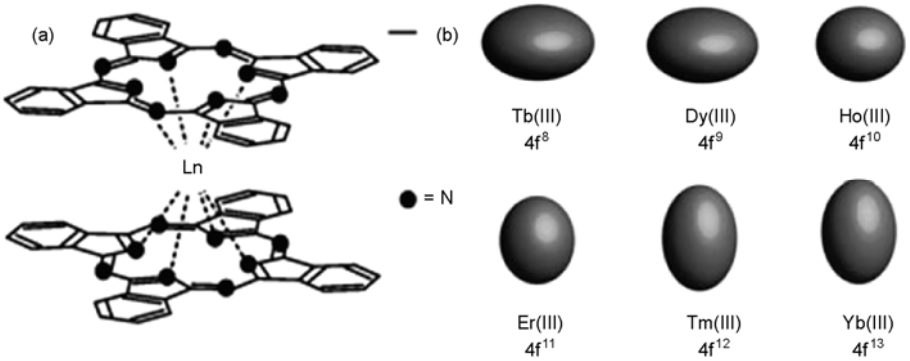

Figure 1 (a) Schematic diagram of the anion $[Pc_2Ln]^-$ in ref. [14]. (b) Quadrupole approximations of the 4f-shell electron distribution for tripositive lanthanides. Adapted from ref. [40]. Copyright 2011 The Royal Society of Chemistry.

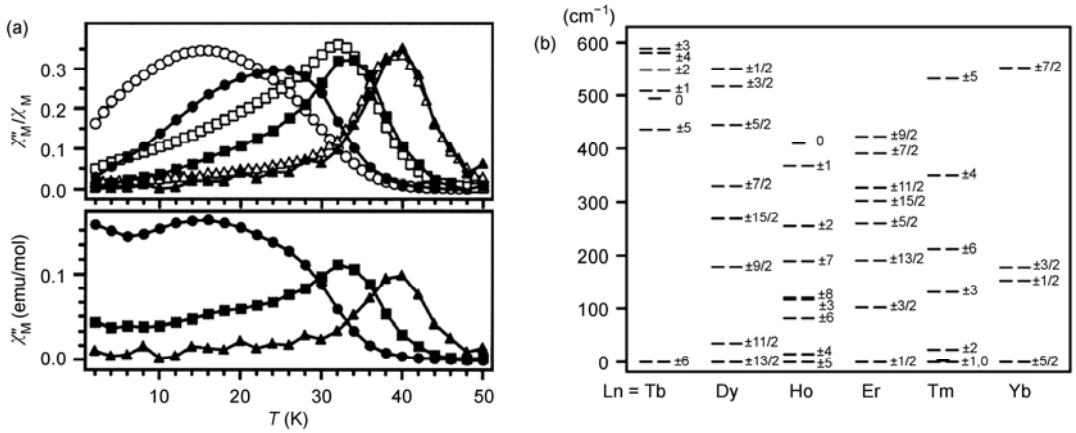

Figure 2 (a) Plots of (top) χ''_M/χ_M and (bottom) χ'' against temperature T for a powder sample of $[Pc_2Tb]^-$complex (open marks) and that diluted in $[Pc_2Y]^-TBA^+$ (filled marks, $[Pc_2Tb]^-/[Pc_2Y]^-$=1/4). Adapted from ref. [14]. Copyright 2003 American Chemical Society. (b) Energy diagram of the substates of the ground multiplets of $[Pc_2Ln]^-TBA^+$ (Ln = Tb, Dy, Ho, Er, Tm, or Tb) determined in ref. [36]. Copyright 2004 American Chemical Society.

χ''_M/χ_M curves shift to higher temperatures in the lower-temperature parts, ensuring the single molecule relaxation behavior because the spin-spin interaction between adjacent molecules is weakened. The energy barrier Δ/k_B has become 230 cm^{-1} with a pre-exponential factor (τ_0) of 6.25×10^{-8} s by an Arrhenius analysis. The complex $[Pc_2Dy]^-$ shows similar slow magnetization relaxation behavior. The fitting of the Arrhenius law obtains an effective energy barrier of 28 cm^{-1} with a pre-exponential factor (τ_0) of 6.25×10^{-6} s. Other lanthanide-based complexes of the same series, except for the $[Pc_2Ho]^-$ complex, have no such slow magnetization relaxation behavior [39].

To elucidate the difference in magnetization behavior for these complexes, the sublevel structures are determined by the simultaneous least squares fitting of paramagnetic NMR shifts and magnetic susceptibility data [36], as shown in Figure 2(b). The large double-degenerate ground states of m_J = ±6, ±13/2, and ±5 are characterized for the Tb, Dy and Ho-based complexes, indicating the presence of a strong uniaxial magnetic anisotropy that results in the slow magnetization relaxation behavior. The energy separation of 400 cm^{-1} between the first and second lowest states for $[Pc_2Tb]^-$ is the largest, which is consistent with the highest anisotropy energy barrier. Recently, Long et al. [40] developed a simple model to interpret the phenomenon (Figure 1(b)). Because of the oblate f-electron charge cloud (equatorially expanded) for Tb^{III}, Dy^{III} and Ho^{III} free ions, a sandwich-type ligand field could maximize the single ion anisotropy, considering the repulsive contacts between ligand and f-electron charge clouds. As a result, the slow relaxation behaviors were observed for the Tb^{III}, Dy^{III} and Ho^{III} complexes but not for the Er^{III}, Tm^{III} and Yb^{III} complexes.

In contrast, an Er-based complex of polyoxometalates (POMs) [41], the sodium salt of the $[ErW_{10}O_{36}]^{9-}$ polyanion, was reported to have SMM behavior, associating with a structure similar to that of $[Pc_2Ln]^-$complexes, as shown in Figure 3(a). The nearest Er–Er distance of 11.225 Å indicates the spin-spin interactions between adjacent molecules are negligible. Consequently, the slow relaxation behavior of magnetization should be considered a single ion property. The skew angle is about 44.2°, which is much closer to an ideal D_{4d} symmetry (Φ = 45°) than $[Pc_2Ln]^-$ (Figure 3(a)). In addition, the square-antiprism built up by the 8-fold coordinated Er^{3+} ion exhibits a certain axial compression (Figure 3(b)), while axial elongation is observed for "double-decker" phthalocyanine complexes. In fact, the Er-based phthalocyanine complex shows no slow relaxation phenomenon, with the low-lying ground states of m_J = ±1/2. Interestingly, through the fitting of the susceptibility data of $[ErW_{10}O_{36}]^{9-}$, a high Kramers doublet ground state with m_J = ±13/2 is present. Possibly it is their hair-like geometrical differences that bring the changes to the LF parameters of a single lanthanide ion, resulting in the distinct magnetization properties for two types of sandwich-like complexes.

2 Magnetic interactions

Besides the intrinsic magnetic anisotropy, the magnetic

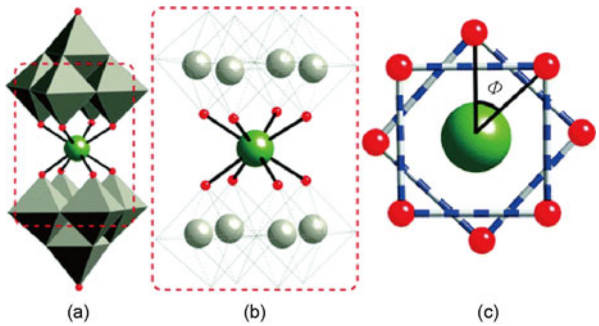

Figure 3 Structure of the $[ErW_{10}O_{36}]^{9-}$ and projection showing the Er^{3+} ion square-antiprismatic coordination site. Adapted from ref. [41]. Copyright 2008 American Chemical Society.

(dipolar and exchange) coupling in the system may mitigate quantum tunneling relaxation processes which shortcuts the anisotropy energy barrier, thus significantly affecting the dynamic magnetic behavior [42,43]. However, because of the internal nature of the f electrons, the interactions in pairs of f electrons are expected to be small, limiting the maximum spin-reversal barrier that can be achieved in lanthanide-containing complexes. Designing lanthanide-containing complexes with strong exchange coupling presents a formidable challenge, but at the same time offers a promising route towards higher relaxation barrier SMMs. Extensive research attempts have been made, such as choosing oxalato-based or non-oxygen (Cl, N) bridging ligands. In 2010, the first oxalato-based lanthanide SMM $[Dy_2(Bpz_3)_4(\mu\text{-ox})]$ ($HBpz_3$ = hydrotris(pyrazolyl)borate; ox^{2-} = oxalate) was successfully synthesized by some of the authors [44]. In addition, a chloro-bridged dinuclear dysprosium SMM compound, $[(\eta^5\text{-Cp})_2(thf)Dy(\mu\text{-Cl})]_2$ (Cp = C_5H_5, thf = tetrahydrofuran), has been synthesized recently by Richard and co-workers [45]. In particular, as a way to address this challenge, Long and colleagues [46] provide one effective means of achieving strong coupling through the use of radical bridging ligands, where the diffuse spin orbitals that can penetrate the core electron density of the lanthanide ions, promote strong exchange coupling.

2.1 $[K(18\text{-crown-6})]\{[(Me_3Si)_2N]_2(THF)Ln\}_2$

N_2^{3-} radical-bridged lanthanide complexes, $[K(18\text{-crown-6})]\{[(Me_3Si)_2N]_2(THF)Ln\}_2$ ($\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2$) (Ln = Gd^{III}, Dy^{III}, Tb^{III}; THF, tetrahydrofuran), were reported by Long and colleagues [46], exhibiting much stronger magnetic coupling than previously obtained lanthanide complexes. The centrosymmetric dinuclear complex is composed of two five-coordinate lanthanide ions bridged by N_2^{3-} ligand, in a pseudotetrahedral configuration (Figure 4(a)).

Direct current (DC) magnetic susceptibility data were fitted using a spin-only Hamiltonian (Figure 4(b)), revealing the parameter of $J = -27$ cm^{-1}, which represents the strongest magnetic coupling between a Gd center and paramagnetic ligand observed for a gadolinium compound. Furthermore, a coupling constant of $J = -0.49$ cm^{-1} was provided by investigating the magnetic properties of the non-radical N_2^{2-} bridged gadolinium compound, confirming that the radical bridge is essential for attaining strong coupling in this system. The Dy^{III}-containing complex shows similar magnetization behavior. These results signal the ability of the N_2^{3-} radical ligand to mediate the strong magnetic exchange coupling between lanthanide ions and suggest that slow magnetic relaxation could arise through a "giant spin" mechanism.

To verify the single-molecule magnetic behavior, variable-frequency alternating current (AC) magnetic susceptibility measurements were performed for the dysprosium analogue, showing a series of frequency-dependent peaks (Figure 5(a)). Relaxation times were extracted through fitting Cole-Cole plots for AC susceptibility collected at a 0 Oe applied DC field. An Arrhenius fit to the data gives an effective relaxation barrier of $U_{eff} = 123$ cm^{-1} with a pre-exponential factor of $\tau_0 = 8\times10^{-9}$ s. In contrast, by measuring variable-frequency AC magnetic susceptibility of the non-radical N_2^{2-} bridged dysprosium compound (Figure 5(b)), an energy barrier of $U_{eff} = 18$ cm^{-1} was shown with a relaxation time constant of $\tau_0 = 2\times10^{-6}$ s. The obvious difference indicates that the anisotropy originates from the concerted effect of the anisotropic Dy^{III} ground states and the strong magnetic coupling through the radical N_2^{3-} bridge.

Recently, further efforts have extended the system to other lanthanide ions [47]. Surprisingly, at an average sweep rate of 0.9 mT/s, an open magnetic hysteresis curve was observed at 14 K with a coercive field reaching 5 T below 11 K for the Tb complex, which displays the highest measured hysteresis temperature in the field of single- molecule magnets. This work provides a promising strategy to design new lanthanide SMMs using radical bridging ligands.

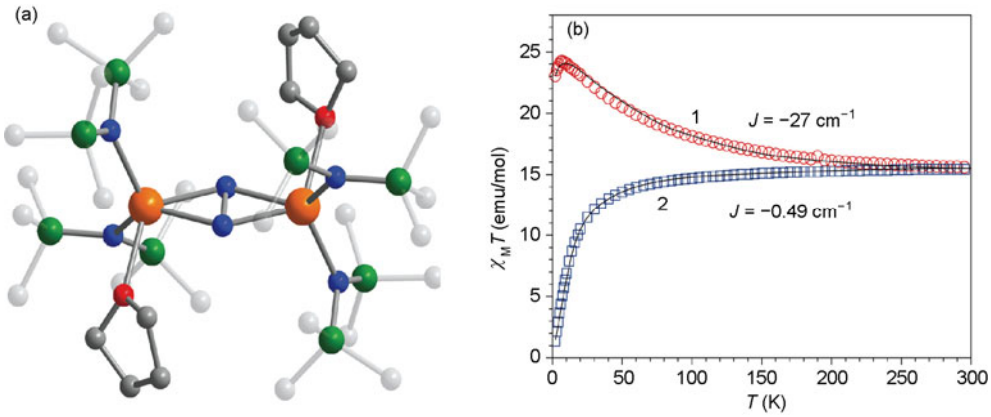

Figure 4 (a) Structure of the $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)^-$ anion. Crystallographic data available in ref. [46]. (b) Variable-temperature molar magnetic susceptibility data (χ_M) for the N_2^{3-} radical-bridged Gd^{III} complex (red circles) and non-radical N_2^{2-} bridged Gd^{III} compound (blue squares). Adapted from ref. [46]. Copyright 2011 Nature Publishing Group.

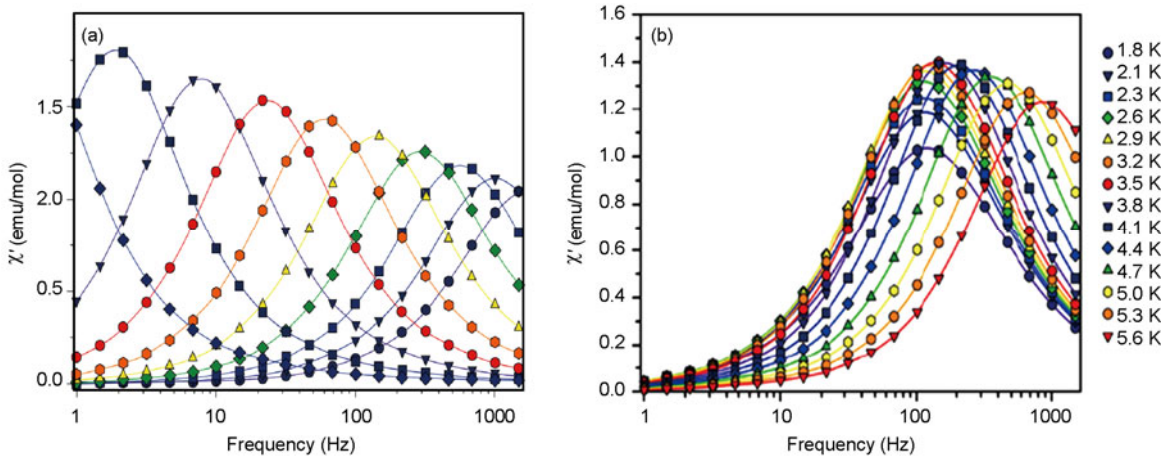

Figure 5 Temperature dependence of the out-of-phase components of the AC magnetic susceptibility for the N_2^{3-} radical-bridged Dy^{III} complex (a) and non-radical N_2^{2-} bridged Dy^{III} compound (b) under zero applied DC field. Adapted from ref. [46].

2.2 Asymmetric Dy_2

In parallel, studies of an asymmetric dinuclear dysprosium compound have shown efficient suppression of quantum tunneling by Ising exchange interaction leading to a long relaxation time in this compound [43].

The complex, $[Dy_2ovph_2Cl_2(MeOH)_3]_3 \cdot MeCN$ (H_2ovph = pyridine-2-carboxylic acid [(2-hydroxy-3-meth-oxyphenyl)-methylene] hydrazide), contains two dysprosium ions with different coordination environments, where the metal centers are bridged by the alkoxido groups of $ovph^{2-}$ ligands with two Dy-O-Dy angles 112.3(2)° and 111.5(2)°. The eight-coordinate Dy1 center exhibits a hula hoop-like geometry, whereas the seven-coordinate Dy2 center has a near perfect pentagonal bipyramidal coordination (Figure 6(a)). The one-dimensional supramolecular chain arrangement is held together by strong intra and intermolecular hydrogen-bonding interactions. The sharp increase of the $\chi_M T$ value at low temperatures suggests the presence of intramolecular ferromagnetic interactions between the metal centers (Figure 6(b)). This compound provides a unique opportunity to simultaneously probe the contributions of the exchange interaction and single-ion anisotropy to the relaxation dynamics of polynuclear lanthanide systems.

AC susceptibility measurements have been performed under a zero-DC field (Figure 6(c)). A series of dependent temperature peaks in the out-of-phase component (χ'') indicate a typical slow relaxation of the magnetization. For most SMMs, on cooling, the increase of χ' and χ'' is often observed in the low-temperature regime, which could be attributed to the quantum tunneling effects at zero DC field. In contrast, both χ' and χ'' components for the complex cascade like avalanches below the blocking temperature and nearly vanish as the temperature approaches 2 K. This signals the "freezing" of the spins by the anisotropy barriers and can be taken as a clear indication of the efficient suppression of the zero-field tunneling of magnetization occurring in this complex.

Ab initio calculations show the local anisotropy axes, corresponding to strongly axial g tensors on the dysprosium sites, are almost parallel to each other. This leads to an Ising type of exchange interaction. Figure 2 shows the calculated $\chi_M T$ for a powder for the set $J = 5.88$ cm^{-1} (each Dy^{III} ion is described as an effective $S = 1/2$ system) and $zJ = -1.84$ cm^{-1}. Through calculating the dipolar contribution to J, a parameter of $J_{dip} = 5.36$ cm^{-1} is obtained, indicating that the ferromagnetic coupling comes almost entirely from a ferromagnetic dipolar interaction. The high axiality and Ising exchange interaction efficiently suppress the quantum tunneling of magnetization of the complex. This is an example of how a strong ferromagnetic interaction between lanthanide ions can be achieved by engineering the local anisotropy axes.

The specific breakthrough of the present study was the clear realization, on the basis of combined experimental and theoretical investigations, of the crucial ingredients necessary to achieve long relaxation times in lanthanide complexes and their relationship to the molecular structure. These are (1) the high axiality of lanthanide sites leading to a preponderant Ising type of interaction between them, (2) the almost parallel local anisotropy axes and (3) the non-negligible exchange interaction between the Dy ions. These three ingredients together contribute to the suppression of the quantum tunneling of magnetization, a precondition for the use of these complexes as elements in nanoelectronics. This provides a promising strategy for enhancing the single-molecule magnet properties of polynuclear lanthanide-based complexes via fine-tuning the local environments of the lanthanide ions.

3 Conclusions and perspective

As a lively crossroad for chemistry, physics, and materials science, SMMs have sparked increasing interest in the area of molecular magnetism, in particular lanthanide metal systems. Remarkable progress is being made regarding the

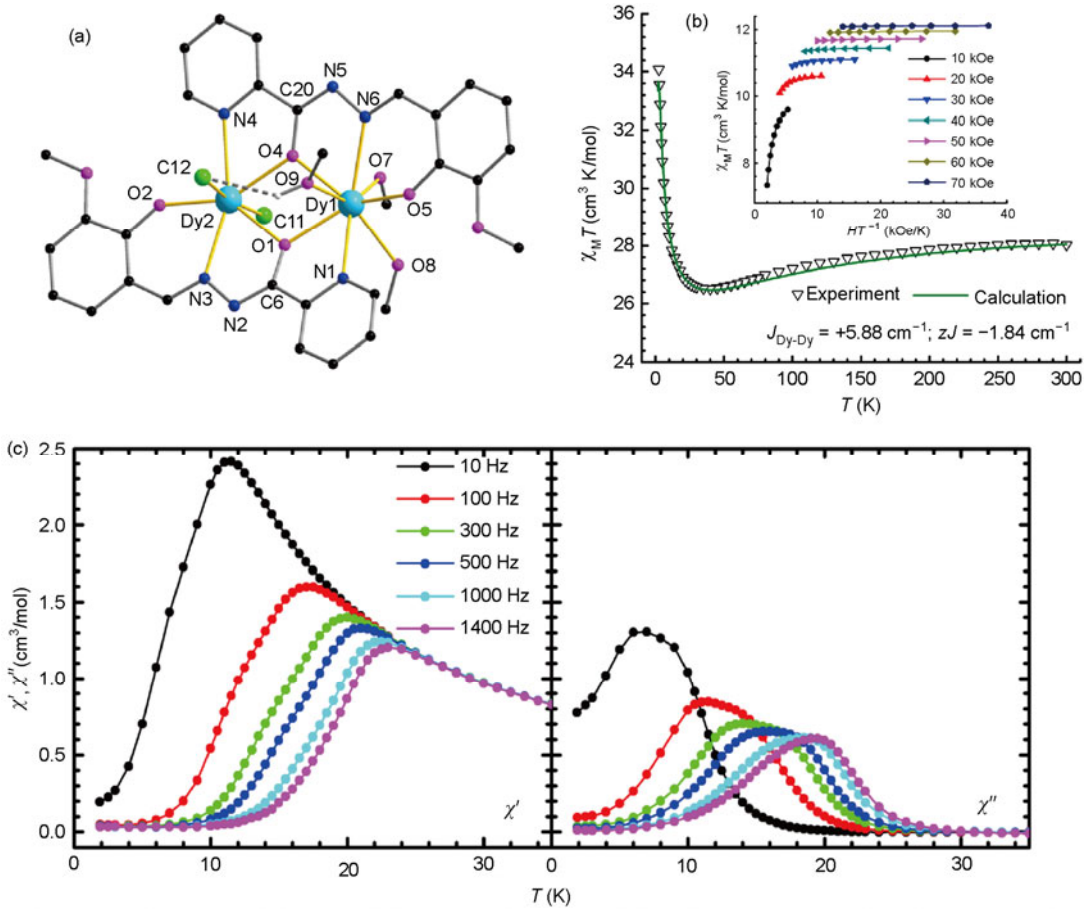

Figure 6 (a) Structure of the asymmetric Dy_2 system. Crystallographic data available in ref. [43]. (b) Variable-temperature molar magnetic susceptibility data (χ_M) for Dy_2. (c) Temperature dependence of the in-phase (χ') and out-of-phase components of the AC magnetic susceptibility for Dy_2 under zero applied dc field. Adapted from ref. [43]. Copyright 2011 American Chemical Society.

synthesis and characterization of lanthanide-based SMMs, but there are several challenges that need to be addressed before we can tap into the full potential of these magnetic nanostructures. In this review article, we have summarized various methodologies for moderating the magnetic relaxation of SMMs and highlighted two main factors, i.e. the crystal field and magnetic interactions. The crystal field plays a dominant role in creating single-molecule magnets with f-elements, and a reliable picture of the electronic structure of lanthanide based systems can be obtained with *ab initio* methods or the classic LF models. In particular, we provide a snapshot of recent progress in magnetic interactions where we have briefly introduced the most important methods for achieving strong coupling (the use of radical bridging ligands). We stress that the interactions (magnetic dipolar interactions, anisotropic exchange interactions and Dzyaloshinsky-Moriya antisymmetric exchange interactions [48]) are not negligible and make a great difference in achieving higher barrier single-molecule magnets [49]. Our experiment and the *ab initio* calculations of other groups suggest that the almost perfect axiality of the ground doublet state and strong Ising exchange interaction are important features enabling lanthanide based systems to function as single-molecule magnets [43,50].

A major goal for chemists has been to design and synthesize molecules retaining functionality in a more readily accessed temperature regime [40]. Notably, the achievement of this goal hinges upon raising the inherent molecular spin-inversion barrier. However, the weak magnetic exchange coupling, concomitant with fast quantum tunneling, limits the maximum spin-reversal barrier that can be achieved in lanthanide-containing complexes. Attempts are presently under way to overcome this difficulty, in particular, the use of *ab initio* methods or the classic LF models is very helpful for investigating the SMM behavior of lanthanide complexes. It is hoped that future *ab initio* or DFT investigations could provide useful clues to predict and elucidate the relationship between the electronic structure and relaxation process. In addition, the use of actinides in molecular magnetism appears timely. Recently, slow magnetic relaxation behavior has been observed with actinide-based complexes, $U(H_2BPz_2)_3$ [51], $[Ac(COT)_2]^-$ (Ac = Np; $COT^{2-} = C_8H_8^{2-}$) [52], which is a good sign that the 5f elements might be promising for the design of SMMs with enhanced barriers.

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